Condensed Matter

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1 Bravais Lattice and simple intro: Chapter 1

1. Bravais lattice made of three primitive vectors(in 3d) and any point on lattice can be gotten to by a combination of primitive vectors

2. **Lattice - Definition:** A lattice is a periodic, regular, array of points in an area of 2d or 3d space.

3. **Basis - Definition:** A basis is an atom or multiple atom configuration associated with each point of a lattice

4. Definitions of Bravais Lattices:

   - An array made up of infinetly many discrete points which when viewed from any of the points appear to be the same

   - All the points with the follwoing position vectors(Primitive)

$$\tilde{\mathbf{R}} = n_1\vec{a_1} + n_2\vec{a_2} + n_3\vec{a_3} \tag{1}$$

   s.t. all the a's are vectors in different planes and the n's are integer values.

   - A set of discrete vectors in independent planes, closed under vector addition

5. three types of main bravais lattice

   - Simple cubic (sc)

   - body centred cubic (bcc)

   - face centred cubic (fcc)

6. Lattice + Basis = Crystal

2 Chapter 2: Bravais Lattice Types

- The choice of primitive vectors in bravais lattice is not unique

- the set of primitive vectors is correct if any point can be described by a sum of these primitive vectors

2.1 Types of Bravais Lattice:

Primitive Vectors are the vectors used to define a bravais lattice

1. **Simple Cubic lattice**
   Has the following primitive vectors:

   $$\vec{a_1} = a\hat{x} \ , \vec{a_2} = a\hat{y} \ , \vec{a_3} = a\hat{z} \tag{2}$$

   inter atomic radius r: $a = 2r$

2. **Body-Centered Cubic**
   Has the following primitive vectors:

   $$\vec{a_1} = \frac{a}{2}(\hat{a} + \hat{y} - \hat{z}) \ , \vec{a_2} = \frac{a}{2}(-\hat{a} + \hat{y} + \hat{z}) \ , \vec{a_3} = \frac{a}{2}(\hat{a} - \hat{y} + \hat{z}) \tag{3}$$

   interatomic radius $a = 4r/\sqrt{3}$

3. **Face-Centered Cubic**
   Has the following primitive vectors:

   $$\vec{a_1} = \frac{a}{2}(\hat{y} + \hat{z}) \ , \vec{a_2} = \frac{a}{2}(\hat{z} + \hat{x}) \ , \vec{a_3} = \frac{a}{2}(\hat{x} + \hat{y}) \tag{4}$$

   inter atomic radius $a = 2\sqrt{2}r$

Coordination Number - Definition: The amount of nearest neighbours to any given point, which will always be the same in any bravais lattice due to periodicity

2.2 Primitive Unit Cell

Definition: The *Primitive Unit Cell* is the volume of the bravais lattice, that when translated through all primitive vectors in said lattice fills up all the space, leaving no voids, or without overlapping.
Mathematical Definition: The set of all points in the following form

$$\tilde{\mathbf{r}} = n_1\vec{a_1} + n_2\vec{a_2} + n_3\vec{a_3} \tag{5}$$

where $\vec{a}_{1,2,3}$ are the set of primitive vectors and the x values range between 0 and 1.

Each primitive unit cell only takes up one point of the bravais lattice, meaning the Volume of primitive cells can be described as
$$V = 1/n \tag{6}$$
where n is the density of points.

2.3 Symmetry Problem

One problem with this method is that it doesn't display full symmetry of bravais lattice, so to combat this we can choose either of the following

1. **Wigner-Seitz Primitive Cell**

   - The region of the space that is closer to the point than it is to any other point, i.e. area within bisection of lines connecting point to nearest neighbours.

2

2. **Conventional Unit Cell**

    (a) Unit cell that fill up all the space without overlapping, when translated through a particular subset of the vectors of the bravais lattice.

3 Chapter 3

3.1 Symmetry Group of Bravais Lattice

(a) Translation through Bravais vectors

(b) Operations that leave a point fixed on lattice Point group subset)

(c) Operations constructed by successively combining 1 and 2

3.1.1 Point Group Subset

Seven Crystal Systems

(a) Cubic

(b) Tetragonal

(c) Orthorhombic

(d) Monoclinic

(e) Triclinic

(f) Rhombohedral

(g) Hexagonal

Point group operations

(a) Rotations

(b) Rotations-Reflections

(c) Rotation-Inversions

(d) Reflections

(e) Inversions

4 Chapter 4: reciprocal Lattice

Bravais lattice are invariant under translation along primitive vectors, which means their properties can be described be periodic function

4.1 Reciprocal Space

The k-space is the space where Fourier transform of a spatial function in represented. This means a Fourier transform takes us from real space to k-space. (For visualisation look at slide 91)

4.2 Reciprocal Lattice

the *Reciprocal Lattice* is the set of all wave vectors which produce plane waves with the same periodicity of bravais lattice

(a) **Definition**

A reciprocal lattice is the set of all the vectors $\vec{\mathbf{k}}$, satisfying $e^{i\vec{\mathbf{k}}\mathbf{R}} = 1$

(b) the first **Brillouin Zone** is the Wigner-Seitz cell of reciprocal lattice

relation between real space primitive vectors and reciprocal lattice vectors

$$bi = 2\pi \frac{a_j \times a_k}{a_1 \cdot (a_2 \times a_3)} \tag{7}$$

4.3 reciprocal lattice volume

If the volume of primitive cell in direct lattice is given by $\mathbf{V}$, then the volume of primitive cell of the reciprocal lattice is given

$$\frac{(2\pi)^3}{V} \tag{8}$$

Reciprocal Lattice vectors

$\bullet$

$$\vec{k} = h\vec{b_1} + k\vec{b_2} + l\vec{b_3} \tag{9}$$

5 Chapter 5: Lattice planes

5.1 Lattice Plane

Definition: a plane containing at least three non co-linear lattice points is defined as a *lattice plane*

- *family of lattice planes:* a set of parallel, equal separation, planes, which together all the points of the three dimensional bravais lattice

5.2 Theorem

(a) For any family of lattice planes, of separation distance d, there exits reciprocal lattice vectors perpendicular to the planes, with the shortest having length: $\frac{2\pi}{d}$

(b) Conversely, for any reciprocal lattice vector $\mathbf{k}$, there exists a family of plane waves normal to it, with separation d, of which $\frac{2\pi}{d}$ is the length of the shortest vector parallel to it

(c)

$$|\tilde{\mathbf{k}}| = \frac{2\pi}{d} \tag{10}$$

5.3 Miller Indices

Definition: the coordinates of the shortest reciprocal lattice vector normal to the specified lattice plane, wrt to a set of primitive reciprocal lattice vectors, is known as the *Miller indices*

- a plane with miller indices h,k,l is normal to a reciprocal lattice vector: $h\vec{b_1} + k\vec{b_2} + l\vec{b_3}$

- as no unique $a_{(1,2,3)} \implies$ no unique$b_{(1,2,3)}$ there are no unique choice of miller indices

- the axes interception is inversely proportional to the miller indices

6 Chapter 6: Bragg and Von Laue

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$$\text{Bragg's Law: } n\lambda = 2dsin\theta \tag{11}$$

- Bragg's Law assumes crystal is made of parallel planes of ions. equally spaced at distace d apart.
  in order to form sharp peaks

  - X rays are specularly reflected

  - X rays forms successive planes interfere constructively

    * path difference between two rays from successive planes is $2dsin\theta$

- θ is half of deflection angle

6.1 Von Laue

- no lattice planes needed

- x-rays from all lattice planes interfere constructively

- The path difference of two rays scattered is

$$dcos\theta + dcos\theta' = \vec{d}(\mathbf{n} - \mathbf{n}') \tag{12}$$

- condition for interference

$$\vec{d}(\vec{n} - \vec{n}') = m\lambda \tag{13}$$

- in order to get a condition for both the incident and scattering wave vectors multiply both sides by $2\pi/\lambda$

$$\vec{d}(\vec{k} - \vec{k}') = m2\pi \tag{14}$$

- now take into account all bravais lattice sites

$$\vec{R}(\vec{k} - k') = 2\pi m \tag{15}$$

6.2 Bragg's Plane

- The tip of the incident wave vector $\vec{k}$ lie on the plane that is perpendicular to the bisector of a line joining origin of the k space to the reciprocal lattice point $\vec{K}$

7 Chapter 7: Bragg and Von Laue Equivalence

7.1 Equivalence of Bragg and Von Laue

- if we choose the lattice plane perpendicular to $\vec{K}$ both $\vec{k}$ and $\vec{k}'$, (which are both of equal magnitude due to elastic scattering), make an angle θ with the plane

- The reciprocal lattice is also a bravais lattice

- $\vec{K}$ is an integer multiple of $\vec{K}_0$, which is the shortest reciprocal lattice vector perpendicular to the plane, i.e.

$$\vec{K} = n\vec{K}_0 \tag{16}$$

- this means

$$|\vec{K}_0| = 2\pi/d \tag{17}$$

and

$$|\vec{K}| = 2\pi n/d \tag{18}$$

- by diagram on pg 174 we know $|\vec{K}| = 2k sin\theta = 2\pi n/d$which means

- $\pi n/d = k sin\theta$ and we know$k = 2\pi/\lambda$ which can only mean one thing

-

$$n\lambda = 2d sin\theta \tag{19}$$

7.2 Reciprocal Space

- Construct incident wave vector $\vec{k}$ in reciprocal space

- draw sphere of radius k as diffraction peaks will occur if sphere cuts through point of reciprocal lattice

- Diffraction peaks of $\vec{K} = \vec{k} - \vec{k}'$ will only occur if $\vec{K}$ gives a point on sphere surface of reciprocal lattice

We can use a non-monochromatic X-ray of λ_1 and λ_2

- we get two spheres:

$$\vec{k}_0 = 2\pi n/\lambda_0 \tag{20}$$

and

$$\vec{k}_1 = 2\pi n/\lambda_1 \tag{21}$$

- Bragg peaks will occur corresponding to reciprocal lattice vectors lying with two spheres

or we can use the *Rotation Method*

- Monochromatic X-ray used

- both sample and X-ray rotated

- for diffraction to happen both the normal of the plane and bisector of source and detector need to be parallel

8 Chapter 8: Geometric structure and atomic form factor

8.1 Geometric Structure Factor

WHAT IF PRIMITIVE CELL IS MADE UP OF MORE THAN 1 SCATTERING SITE???
this means there is more than 1 atom per site

- the atoms act as identical scattering sites at positions $d_1, ..., d_n$ in the primitive cell

- the rays from all these sites interfere

- phase difference for Bragg peak associated with $\vec{k} - \vec{k}' = \vec{K}$, means the phases of the scattered rays at sights d_i and d_j will be $\vec{K}(d_i - d_j)$

- this means the phase difference of the amplitude of the two rays will differ by *a factor*

$$e^{i\vec{K}\cdot(\vec{d_i}-\vec{d_j})} \tag{22}$$

- the net ray of all these sites will have a factor of all the individual rays from all the sites in the primitive cell, called the *Geometric Structure Factor*

$$S_{\vec{k}} = \sum_{j=1}^{n} e^{i\vec{K}\cdot\vec{d_j}} \tag{23}$$

- this is just the extent to which the interference os waves scattered from identical ions in primitive cell can lower the intensity of Bragg peak of $\vec{K}$

9 Chapter 9

9.1 Defects

- Most Crystal Patterns contain defects

- Defects can be defined as: variation or alteration which ruins the periodicity of bravais lattice at certain points in lattice

- there are to types of defects:

  - *Point defects:* at specific points in lattice. i.e.

    * missing atoms

    * another atom present at site

    * atom located in between lattice sits

  - *Line Defects:*

    * can either be edge dislocation or screw dislocation

      · edge dislocation: extra half plane of atoms introduced to crystals mid way through crystal

      · Screw dislocation: Dislocation in which atomic planes are offset which forms a spiral ramp around line of dislocation (see on pg 223)

    * often occur around boundary between crystals

- Defects are either intrinsic or extrinsic

  - Intrinsic

    * Intrinsic means it is integral to crystal structure

    * they don't change overall composition

  - Extrinsic means the crystal has been externally manipulated, or foreign atoms have got in

9.2 Epitaxy

Crystalline materials can be grown by *Epitaxy*

- Monocrystalline film (which is the epitaxy layer) is deposited on monocrystalline base(substrate)

- the epitaxial layer copies structure of base below it

chapter 12: Density of States

Sound is a good example of propagation of treating a material as a continuum as the wavelength is much bigger than then interatomic distance.

- Take a 1d plane wave $u_x = (x,t) = u_x^0 e^{[i(kx - \omega t)]}$

- phase velocity $v_\phi \equiv \omega / k$

- group velocity $v_g = \partial \omega / \partial k$

in a cube of length side L

- when

$$\lambda = 2L; \quad k = \frac{\pi}{L} \text{ x } 1 \tag{24}$$

- when

$$\lambda = L; \quad k = \frac{\pi}{L} \text{ x } 2 \tag{25}$$

- when

$$\lambda = \frac{2L}{3}; \quad k = \frac{\pi}{L} \text{ x } 3 \tag{26}$$

In 1d case

- allowed K_i^s are discrete points spereated by a distance of π / L

Density of States

Volume in k-space which corresponds to one k-value is

-
$$v_k^s = (\frac{\pi}{L})^3 = \frac{\pi^3}{V} \tag{27}$$

- from this we can see the number of k-values in unit volume of k-space is

$$\rho_k^s = \frac{V}{\pi^3} \tag{28}$$

- this means the number of distinct standing wave states (k-values) for a given polarisation type is the volume and thickness multiplied by the k space density

- $g_i(k)$ is the density of states in the k space

$$g_i(k)dk = \frac{1}{8}\frac{V}{\pi^3}4\pi k^2 dk = \frac{Vk^2 dk}{2\pi^2} \tag{29}$$

- but also can be written in terms of frequency

$$g_i(k)dk = g_i(\omega)d\omega \tag{30}$$

- as we know $v_\phi \equiv \omega/k$ and $v_g = \partial\omega/\partial k$

$$g_i(k)dk = \frac{Vk^2}{2\pi^2}dk = \frac{(V\omega)^2}{\underline{}} \tag{31}$$

Total Vibrational density of States

there is one Longatudinal acoustic and two tranverse acoustic

$$g(\omega)d\omega = \frac{V\omega^2}{2\pi^2}(\frac{1}{v_l^3} + \frac{2}{v_t^3})d\omega = \frac{3\omega^2 V}{2\pi^2 v_0^3}d\omega \tag{32}$$

where v_0 is the average defined on pg 290

9.3 Debye Frequency

As there are N atoms in a sample, each with three degrees of freedom, we can say there are 3N degrees of freedom in the sample

- we call that max frequency the Debye frequency (as he discovered it)

- by integrating the density of states by the width over all the allowed frequencies will be equal to 3N

$$\int_0^{3N} g(\omega)(d\omega) = 3N \tag{33}$$

- and

$$\int_0^{\omega_D} g(\omega)(d\omega) = \frac{3V}{2\pi^2 v_0^3}\int_0^{\omega_D}\omega^2 d\omega \tag{34}$$

- we can get

$$\omega_D = (\frac{6\pi^2 N}{V})^{1/3}v_0 \tag{35}$$

Chapter 13

- interatomic separation defines lower limit for λ and there defines the upper limit for k

- allowed k values

$$K_i^r = 0 \pm n_i\frac{2\pi}{L} \tag{36}$$

- this means the density of running waves is

$$\rho_k^r = \frac{V}{8\pi^3} \tag{37}$$

- which means number of states for a given polarisation between k and k+dk is

$$g_i(k)dk = \frac{V}{8\pi^3}4\pi k^2 dk = \frac{Vk^2 dk}{2\pi^2} \tag{38}$$

Chapter 14: 1-D monatomic Chains

- if the distance between atoms is a and if atomic interaction energy is $\phi(a)$ the total chain potential energy is

$$U = N\phi(a) \tag{39}$$

- displacement from equilibrium $= u_{n-i}$ where i is the amount of wavelengths past 1 it is displaced

- energy change from displaced atoms is seen as the change in elastic energy of a spring inserted between neighbouring atoms

$$U^{harm} = \frac{1}{2}\mathbf{K}\sum_n (u_n - u_{n+1})^2 \tag{40}$$

where $\mathbf{K}$ = spring constant =

- general form of energy of a chain is

$$U = N\phi(a) + \sum_{m \geq 1}\frac{1}{m!}\frac{\partial^m \phi}{\partial u^m}\sum_n^N (u_n - U_{n+1})^m \tag{41}$$

- $\frac{\partial \phi}{\partial u} = 0$ as atoms are close to equilibrium

Vibrational Frequencies

- return to harmonic vibrational energy approximation

$$M\frac{\partial^2 u_n}{\partial t^2} = -\frac{\partial U^{harm}}{\partial u_n} = -\mathbf{K}(2u_n - u_{n+1} - u_{n-1}) \tag{42}$$

- we need solution in the form of a superposition of harmonics

$$u_n(t) = \sum_k u_k^0 e^{i(kx_n^0 - \omega_k t)} \tag{43}$$

- the k values are from before as $k_i^r = 0 \pm n_i(\frac{2\pi}{L}$ up to $\frac{N\pi}{L}$
- $na = x_n^0$
- back to this equation we get

$$-M\omega_k^2 u_k^0 e^{i(kna - \omega_k t)} = -\mathbf{K}u_k^0(2e^{i(kna - \omega_k t)} - e^{i(k(n+1)a - \omega_k t)} - e^{i(k(n-1)a - \omega_k t)}) \tag{44}$$

the minus in front of the m comes from bring the i down when taking the derivative

- which gives

$$-M\omega^2 u_k^0 e^{i(kna - \omega_k t)} = -\mathbf{K}u_k^0 e^{-i\omega_k t}(2e^{ikna} - e^{ik(n+1)a} - e^{ik(n-1)a}) \tag{45}$$

find rest of derivation in gallery

Velocities

- phase velocity is velocity of individual wave
- group velocity is velocity of wave packet, i.e. with interference from all small waves in packet

Chapter 16: 3D - Crystals

Branches

- acoustic and optic branches in $\omega(k)$ dispersion
- for N primitive cells, p atoms per cell $\implies$ **3pN degrees of freedom** per crystal, i.e. 3 per atom
- each branch has N allowed k values $\implies$ 3p branches
- of these 3 modes are acoustic
    - 1 longitudinal
    - 2 transverse
- $\implies$ 3p-3 optic modes
    - (p-1) are longitudinal optic
    - (2p-2) or transverse optic

Chapter 21: Electron's in Periodic Solids

- Free fermi electro gas model only works for metals, not semi conductors or insulators
    - measuring of mass of current carriers can show $m \neq m_e$

Bloch's Theorem

- atoms with position
$$\vec{R}_n = u\vec{a} + v\vec{b} + w\vec{c} \tag{46}$$
where a,b,c are bravais lattice vectors and u,v,w are primitive vectors
- due to periodicity
$$\begin{aligned} \Psi(\vec{r} + \vec{a}) = A\Psi(\vec{r}) \\ \Psi(\vec{r} + \vec{b}) = B\Psi(\vec{r}) \\ \Psi(\vec{r} + \vec{c}) = C\Psi(\vec{r}) \end{aligned} \tag{47}$$
where A,B,C are phase factors. these describe the wave function at neighbouring sites
- We can imagine a parallelepiped with sides : $N_1\vec{a} + N_2\vec{b} + N_3\vec{c}$

- by Born Von Karman we get

$$\Psi(\vec{r} + N_1\vec{a}) = \Psi(\vec{r}) = A^{N_1}\Psi(\vec{r})$$
$$\Psi(\vec{r} + N_2\vec{b}) = \Psi(\vec{r}) = A^{N_2}\Psi(\vec{r})$$
$$\Psi(\vec{r} + N_3\vec{c}) = \Psi(\vec{r}) = C^{N_3}\Psi(\vec{r})$$

$$(48)$$

- this implies

$$A^{N_1} = B^{N_2} = C^{N_3} = 1 \tag{49}$$

- this means for A,B,C , but here we will just look at A

$$A = e^{2\pi i n_1/N} \tag{50}$$

where $n_1 = 0; \pm 1, \pm 2, ...$

- we can now write this as

$$1 = e^{i\vec{k}N_1\cdot\vec{a}} = e^{i\vec{k}N_2\cdot\vec{b}} = e^{i\vec{k}N_3\cdot\vec{c}} \tag{51}$$

- here

$$\vec{k} = g_1\vec{a}^* + g_2\vec{b}^* + g_3\vec{c}^* \tag{52}$$

-

$$g_1 = \frac{n_1}{N_1}, \ g_2 = \frac{n_2}{N_2}, g_3\frac{n_3}{N_3} \tag{53}$$

with all $g_i's < 1$.

- this means importantly

$$\Psi(\vec{r} + \vec{R}) = e^{i\vec{k}\cdot\vec{R}}\Psi(\vec{R}) \tag{54}$$

- and equivalently

$$\Psi_k(\vec{r}) = e^{i\vec{k}\cdot\vec{r}}u_k(\vec{r}) \tag{55}$$

- where

$$u_k(\vec{r} + \vec{R}) = u_k(\vec{r}) \tag{56}$$

- **ALL THIS MEANS** wave function in a periodic potential is modulated plane wave